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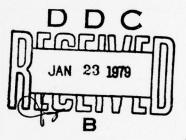
MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

Third Quarterly Progress Report

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Dr. Louis L. Pytlewski

July 1977



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sweat solutions or solutions of the individual components were injected into the column to determine whether the charcoal would preferentially adsorb one or more components thus pinpointing the 'poisoning' material or materials present in synthetic sweat. Conclusions from the studies were that other than loss of capacity of the charcoal due to water, no single component or components could be identified as 'poisoning materials.' Specific conclusions from the static test data were that pretreatment of charcoal with silicone, crown ether, or pH 7 buffer solution all were effective in moderating the reduction of carbon tetrachloride pick up due to exposure to synthetic sweat. This was probably because the pretreatments protected the charcoal from contact with water in the synthetic sweat solutions. Results of the gas chromatography studies were inconclusive.

### **PREFACE**

The work reported in this document was authorized by Task 11762710A09506, Body Protection Investigations. It was carried out from January 1976 to April 1976.

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### I. INTRODUCTION

A substantial number of investigations have been conducted on this problem during the past twenty five years by Edgewood Arsenal personnel and outside contractors. Cverall it is impossible to draw reasonable, workable conclusions from all of the published work heretofore presented. A great deal of the research is at best piecemeal and one often meets contradictions between investigators and within particular publications. Synthetic sweat formulations have been developed and there are significant variations in not so much the types of compounds but in their relative concentration, ".the formulations have included body (sebaceous) oils. The substances present in largest amounts and common to most formulations are inorganic salts such as NaCl, KCl, Ca3(POL)2, CaCO, and KHCO. The organic material common to all formulations is lactic acid--but lower in concentration than NaCl by a factor of 0.05. Also common to all formulations as organic components and in concentrations approximately 10% of the lactic acid are urea, uric acid, formic acid, and glucose. Some formulations also contain very small amounts of organic acids particularly of the amino acid type and these number about twenty different kinds.

The great bulk of sweat studies were conducted using "synthetic sweats" and out of these have evolved two "schools of thought" about the effect of sweat on activated carbon. "School 1" propounds that it is not a "poisoning" which occurs but simply a matter of filling up the internal pores and covering over adsorptive sites in a carbon with sweat solution. From this approach the most often suggested cure for this problem centers on making the carbon hydrophobic yet retaining its gas adsorption capability. "School 2" says that there is a specific ingredient or collection of ingredients in sweat which poison (destroy) the internal adsorptive surface of a carbon. Attention here has focused on lactic acid. Obviously, the solution to this problem is to prevent lactic acid (and/or other "poisons") from getting to the activated carbon.

#### II. EXPERIMENTAL WORK AND RESULTS

Experiments were conducted in two areas of analysis;
a. static tests -- Lost of the experimental work done involved exposure of granular activated carbon (PAC lot 7502) to various solutions and vapors using carbon tetrachloride (CCl<sub>h</sub>) vapor adsorption as an indicator of loss in activity. b. Additionally, dynamic measurements were attempted using gas chromatography wherein columns were packed with activated carbon and sweat samples of various types (especially aqueous lactic acid) were injected onto the column.

\*Owens, C., Private Communication, December 20, 1974

## A. Static Tests

The static tests conducted involved using an enormous number of samples, typically sextuplicates for each experiment, along with controls for each kind of treated carbon. Experience has clearly shown that usual analytical procedures of duplicate and triplicate runs on a single sample are by no means enough when handling activated carbons. Enormous variations in a single batch of activated carbon have more often than not resulted in significant irreproducibility. It is strongly suspected that much of the earlier work on the sweat problem did not take this into account. (We have done copper and chromium analyses on ASC Whetlerite and found analytical deviations of ±10% between samples as large as 100 grams.) In this work, on many occasions control samples of FAC Lot 7502 have shown as high as a 50% variance in CCl<sub>h</sub> vapor uptake on a dry, untreated basis. Everything possible was done in an attempt to limit the effects of the intrinsic heterogeneity of activated carbon.

A typical experiment in our static system was conducted as follows: six, ten gram (g) samples of activated carbon were first heated at 110°C to constant weight at room temperatures. These samples were immersed in a synthetic sweat solution for ten minutes, dried at 70°C for 12 hours, reweighed to check for retained solution and then exposed to CCl<sub>h</sub> vapor in a desiccator for a 24 hour period after which the CCl<sub>h</sub> uptake was determined. Carbon samples were, at times, doubly soaked or treated successively with several solutions and distilled water with subsequent CCl<sub>h</sub> uptake determined. Activated carbons were on occasion also pre-treated with a hydrophobic silicone surfactant and various buffer solutions then exposed to sweat solutions and CCl<sub>h</sub> vapors. The following Table contains information (from left to right) as to type of treatment in column 1; column 2, grams of CCl<sub>h</sub> taken up per gram of carbon (dry); column 3, grams of sweat retained after drying per gram of carbon (dry); column 4, grams

number in column 2 x (number in column 5) x 100

of water retained after drying per gram of carbon (dry); columns 5 and 6, ratio of CCl<sub>1</sub>, uptake to weat retained; column 7, an activity of treated carbon index arrived at by the following:

where 0.842 is the  $\frac{\text{g CCl}_{l_{\downarrow}}}{\text{g carbon dry}}$  for plain, activated, dry carbon. The higher this number, the better the carbon responds after treatments. All carbons were PAC Lot 7502.

Table

Sweat Degradation Experiments on Various Treated and Untreated Carbons

Carbon resistance to sweat and/or H <sub>2</sub> O				•	2690 2644 8655644 86556444	532	108 86
E CC14 E H20							
$\frac{\mathcal{E}   \text{CCl}_{m{\mu}}}{\mathcal{E}   \text{sweat}}$					0.000000000000000000000000000000000000	6.35	2.14
g H <sub>2</sub> 0 g carbon dry							
g sweat g carbon dry					000000 1100 1100 1100 1100 1000 1000 1	0.111	0.200
g CC1 $_{l\mu}$ g carbon dry	0.842		0.557 0.427 0.481		00000 64400 64400 66400 6610 66	0.705	0.427
Type of Treatment	1) FAC 7502; no treatment Reference car- bon	2) Siliconized outer surface coating	HO HO SWOOD	prograted with individual substitution of synthetic sweat-dried at 70°C then sweat treated	a) Uric acid b) Lactic acid c) Formic acid d) CaCO e) KHCO f) NaCl f) NaCl Synthetic z	h) HgC, then	sweat i) Urea j) 1-serine

Table, Continued

Type of Treatment	8 CC14	g sweat	S H20	E 0014	g 0014	Carbon
	g carbon dry	g carbon dry	g carbon dry	g sweat	g H <sub>2</sub> 0	resistance to sweat and/or H20
3) Continued						
c) dl-alanine l) l-aspartic	0.481	0.095	•	5.06		289 407
	0.286	0.02		7 0		421
o) 1-proline	0.250	0.057		200		130
<pre>p) l-histidine b) l-arginine</pre>	0.214	4-1		0,00		41 46
-	0.211	.24		ω, α		22
s) l-lysine t) dl-citrulline	0 0	2.2		J. (.)		\$\frac{1}{2}
1-valine	0.320	4.0		9,		25
<pre>v) 1-leucine w) d1-phenylala-</pre>	0.283	024		4.5		890 890
~	0.207	0.155		1.34		
y) glycine	20	<b>77.</b>		•		
<pre>#) FAC 7502 (pre- trented with pH 10 buffer)</pre>						
a) Controlno	0.415					
other treat-						
b) Synthetic	0.313	0.198		1.58		59
swear treaved c) H2O treated; n6 sweat	0.345		0.1444		2.40	86

Table, Continued

Carbon resistance to sweat and/or H2C			82 33 25 25	14 24 110 110	2000
g cc14 g H20				•	
g ccl <sub>lt</sub>			2.00 1.10 1.00 0.00 0.00	00496 04404 04404	nnon
g li <sub>2</sub> 0 g carbon dry					
g sweat g carbon dry			0.131 0.276 0.241 0.266	0000 0000 0000 0000 0000 0000 0000 0000 0000	60011
$\varepsilon$ CC1 $\psi$		0.382	0000 0000 0100 0100 0000 0000	00000 00000 0000 0000 0000 0000 0000	があるが
Type of Treatment	5) PAC 7502; im- pregnated with selected indi- vidual compo- nents and dried at 52°C then sweat treated	a) Control-no treatments b) Control-no	c) d1-citrulline d) 1-histidine e) 1-leucine f) d1-phenylala-	d d-ribose h) clycine i) glucose j) Lactic acid k) 1-proline	~~~

Table, Continued

Carbon resistance to sweat and/or H <sub>2</sub> O	105	334 158	
g cc1 <sub>μ</sub> g H <sub>2</sub> 0	2.60	6.02	
g CCl <sub>4</sub> g sweat	1.87	3.31	
g H <sub>2</sub> 0 g carbon dry	0.131	0.078	
g sweat g carbon dry	0.162	0.121	
${\it g}$ carbon dry	0.397 0.341 0.303	204°0 294°0 245	0.551
tment	b) PAC 7502; pre- treated with pH 10 buffer- a repeat of #4: above a) Controlno treatments b) H <sub>2</sub> 0 soak only c) Synthetic sweat only	7) FAC 7502; pre- treated with pH 7 buffer a) Control-no sweat or H <sub>2</sub> 0 soaking b) H <sub>2</sub> 0 soak only c) Synthetic sweat only	0) Random con- trolclean PAC 7502 (CCl <sub>t</sub> only)

Table, Continued

Carbon resistance to sweat and/or H,C	7		86 545			221 88			993 2221
g cc14			2,42			5.98			37.0
g CC14 g sweat			1.74			2.76			77.3
g H20 g carbon dry			0.124			0.052			900.0
g sweat g carbon dry			0.150			260.0			0.003
$\varepsilon$ CCl $_{\mu}$		0.375	0.300		0.329	0.311 0.269		0.240	0.226 0.242
Type of Treatment	9) PAC 7502; pre- treated with pH 3 buffer	a) Control-no sweat or H20	boaking b) Mo soak only c) Synthetic sweat only	10) PAG 7502; pre- treated with pH 1 buffer	a) Controlno sweat or H <sub>2</sub> 0	soaking b) H <sub>0</sub> C soak only c) Synthetic sweat only	11) FAC 7502; pre- treated with Dibenso-18- crown-6 ether	a) Controlno sweat or H <sub>2</sub> O	scaking b) H <sub>2</sub> O scak only c) Synthetic sweat only

Table, Continued

Carbon resistance to sweat and/or H <sub>2</sub> C		369 252	19867 3075	5042 76534
8 0014 8 1120		3.83	204.5	602.7
S COLL S sweat		2.78	32.0	32.5
${\cal E}$ ${\cal H}_2$ 0 ${\cal E}$ carbon dry		0.212	†00°0	0.001
g sweat g carbon dry		0.274	0.025	0.019
g CCL <sub>h</sub> g cardon dry		0.036 0.812 0.753	0.00 0.00 0.00 0.00 0.00	0.751 0.643 0.623
Type of Treatment	12) FAC 7502; a control, a in soaked, a synthe-tic sweat soaked carbon were placed in a drying oven at 52°Cafter the days indicated corption measurements were made	1) One day at 52°C 1. Control 2. H <sub>0</sub> only 3. Sheat only	b) Four days at 52°C 1. Control 2. II. conly 3. Effect only	c) Fixe days at 52°C Control 2. II,0 only 3. Sweat only

Table, Continued

carbon dry

Table, Continued

$\epsilon \frac{g  GOl_{L}}{g  H_2^{O}}$ Carbon resistance to sweat and/or $H_2^{C}$	*	78.9 5913	102.3 7450 2011	1889
8 0014 8 8weat		28.6	29.1	25.2
g H20 g carbon dry		0.003	900.0	
g carbon dry		0.021	0.020	0.025 sweat)= -4.5%
g CCl <sub>ll</sub> g carbon dry		0.00 0.634 0.601	0.605 0.614 0.532	631 631 631 631
Type of Treathout	13) Continued c) Sig days at	52 C 1. Control 2. H <sub>2</sub> C only 3. Sweat only	d) Eight days at 52°C 1. Control 2. Ho only 3. Sweat only	o) Elgven days at 520 1. Control 2. H2C only 3. Sweat only 0 Note: sweat (plain H2

# B. Gas chromatography, carbon, and sweat.

It was felt that packing a gas chromatographic column with granular activated carbon and injecting sweat solution and components of synthetic sweat solutions onto the column might result in a workable partitioning. Such could allow for a determination, under dynamic flow conditions, of the relative retention times of the important species present, especially in real human sweat. It was found that a ½" 0.D. stainless steel column shortened to six inches in length was necessary to get anything to arrive at the flame ionization detector. This response did not occur until the column temperature reached approximately 250°C. It was obvious that the one rather broad band we obtained was due to decomposition of several organic compounds in our synthetic sweat sample.

### III. DISCUSSION

In almost every experiment the synthetic sweat solution produced a reduction in the CCl<sub>\(\hat{\mu}\)</sub> adsorptive capacity of an activated carbon which was only slightly larger than that of water alone. At no time, however, could one be inspired to use the word "poisoning." Typically, a loss of 4.5% of adsorptive capacity occurred due to sweat treatment when compared to the effects of water alone on PAC 7502 carbon. Two sets of experiments were conducted wherein the sweat residuals were allowed, at 52°C, to sit in the carbon over a period of 10 to 12 days. At the same time dry controls, and carbons treated with distilled water were run alongside the sweat treated carbons. The CCl<sub>\(\hat{\mu}\)</sub> adsorption for all three types of samples exactly paralleled each other over this time period; the difference appearing only as retained solids in the sweat treated carbon.

Furthermore, aqueous solutions of lactic acid did not produce any sign of a deleterious effect on activated carbon studied and, if our system of classification as shown in columns two and seven of the table has any meaning we would have to place lactic acid in a neutral category. Column seven contains a number for each individual experiment in an attempt to indicate a degree of resistance to removal of adsorptive capacity by a particular kind of treatment or sequence of treatments; the higher the number, the greater the resistance to degradation by the carbon. Large numbers are not as significant in extracting useful information from the experiments as extremely small numbers—numbers less than 100. With this in mind it is noticed that a preponderance of such numbers are obtained for a large percentage of the amino acids, wric acid, and formic acid. Column seven also shows that in a study of the effect of ph buffered carbon on synthetic sweat using ph 10, 7, 3, and 1 buffers that the ph 7 buffer clearly stands out as significantly better than the rest.

Two experiments were conducted using pretreated carbons; one coated with a silicone grease only on the outer surface of the carbon granule, the other impregnated with an organic "molecular sieve" compound called Dibenzo-18-crown-6-ether. It was felt that the crown ether might exclude water and many sweat compounds from the micropores but still allow for unhin-

dered gaseous adsorption.

The silicone treated carbon again showed up well in resisting water adsorption, especially the water in synthetic sweat solutions. Previous experiments involving this degree of success were indicated in the second quarterly report. Hany former studies report on the use of hydrophobic silicone coatings with variable success.\*,\*\*,\*\*\* It is felt that the wide variation in results of such earlier studies was due to the use of silicones in solution or as adsorbed gases which result in plugging up the carbon's internal pores to varying degrees. It is strongly suggested that more attention be given to the use of externally applied hydrophobic surface coatings as a means of at least delaying the effects of sweat.

Although the crown ether impregnated carbon showed a drop off in adsorption of CCl<sub>b</sub> on a dry carbon of about 70% it is noteworthy that synthetic sweat and water were hardly retained by this carbon and the value in the table, column seven is extraordinarily large for the synthetic sweat treated carbon. With more time it is felt that significant overall improve-

ments could be made here.

Hore attention should be given to a complete chromatograinic study of sweat and carbon. Recent advances in instrumentation in an area called "High Pressure Liquid Chromatography" should produce very useful results in the entire sweat problem.

In conclusion, we have not observed anything one could call a unique "sweat poisoning" associated with degradation of activated carbon by the components of synthetic sweat, other than acid degradation, and this is already well known in the

chemistry of activated carbons.

Aqueous lactic acid appears to be entirely neutral in its effect on CCl<sub>k</sub> adsorption by tested activated carbons. Given the right conditions, hydrophobic coatings, such as silicones and fluorocarbon surfactants, should produce a carbon which significantly resists sweat degradation.

<sup>\*</sup> Brillinger, J.H. Report on Active Duty Training. SAREA-DE-DP, September 6, 1972

<sup>\*\*</sup> Brillinger, J.H. Report on Active Duty Training. SAREA-DE-DP, September 25, 1973

<sup>\*\*\*</sup> Warren, R. Inhouse Report. Chemical Sweat Poisoning Study, April-Lay, 1973

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